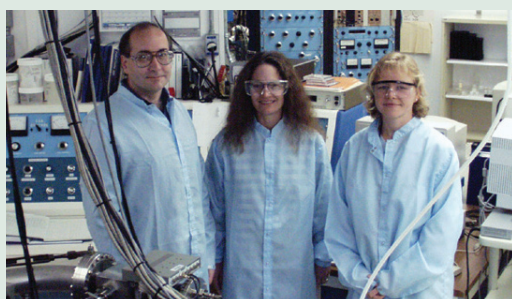


Incorporation of Uranium with Iron Oxide Minerals

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The transport and biological availability of the toxic, radioactive element uranium (U) towards reduction to the less soluble U(IV) species may be limited by co-precipitation with Fe-oxide minerals. We examined the interaction dynamics between U(VI) and iron (Fe) oxides during crystallization by synthesizing Fe-oxide phases [0.5-5.4 mole %U/(U + Fe)] using U(VI) and Fe(III) solutions. Our studies show that U^{6+} is incorporated in Fe oxides as the uncommon uranate species (without axial O atoms) until saturation is reached, whereby U(VI) forms crystalline $U(IV)O_2^{2+}$ phases.



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The geochemical speciation of uranium (U) influences its movement and biological availability in the environment. This information is often used to predict nuclear waste repository performance.

In oxidized environments, U exists as the highly soluble uranyl [$U(VI)O_2^{2+}$] species with two axial U=O double bonds at ~ 1.8 Å. In contaminated materials, solid phase U(VI) typically exists as the uranyl mineral, schoepite [$UO_3 \cdot 2H_2O$]. Uranium(VI) can also exist as the less common uranate solid phase, which has at least three single U-O bonds and no axial double bonds. However, uranates have not been found in nature. The environmental mobility of U is influenced by many processes (**Figure 1**). Another process that may influence U mobility is co-precipitation with other host minerals (**Figure 1**). Uptake of U and other metals occurs during the formation of crystalline and amorphous Fe oxides but the local structure of U in these oxide materials has not been characterized.

Leaching of the synthetic U-Fe oxides typically removed most sorbed and solid phase U(VI) species, leaving on average ~ 0.6 mol % U. X-ray diffraction and infrared spectroscopic studies (**Figure 2A-B**) indicate that hematite (Fe_2O_3) formation is preferred over that of goethite ($FeOOH$) when the U level in the Fe-oxides exceeds 1 mol % U. Our studies with unleached U/Fe solids indicate a relationship between the mol % U in the Fe oxide, and the existence of the spectral features that can be assigned to uranyl species. These spectral features were undetectable in leached solids, suggesting solid phase and sorbed $U(VI)O_2^{2+}$ species are extracted by leaching. Using uranium X-ray Absorption Fine Structure (XAFS) at NSLS beamlines X23A2 and X26A, analyses of unleached solids containing <1 mol % U revealed that U(VI) exists with four O atoms at radial distances of 2.21 and 2.36 Å and Fe atoms at 3.19 Å (**Figure 2C**). Due to the large size of UO_2^{2+} (~ 1.8 Å) relative to Fe^{3+} (0.65 Å), the UO_2^{2+} ion is unlikely to substitute for the Fe. Our results indicate that U^{6+} (~ 0.72 -0.8 Å) is incorporated in the Fe oxides as uranate until a point of saturation is reached. Beyond this concentration, excess U precipitates as crystalline U(VI) phases resembling schoepite.

In summary, our findings indicate that the long-term association of U in the contaminated environment could result in the structural incorporation of U in Fe oxide host phases. In nature, precipitation of pure U phases should occur at a kinetically faster rate than the structural

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incorporation of U into Fe oxides. Precipitation of U as pure mineral phases should be favored at high dissolved U concentrations, whereas sorption and co-precipitation of U are most likely favored at lower U concentrations. In aged, U-contaminated Fe-rich soils, uptake of U by Fe oxides may be significant since ~1 mol % U can be incorporated. The importance of these mechanisms in U-contaminated materials has not been estimated.

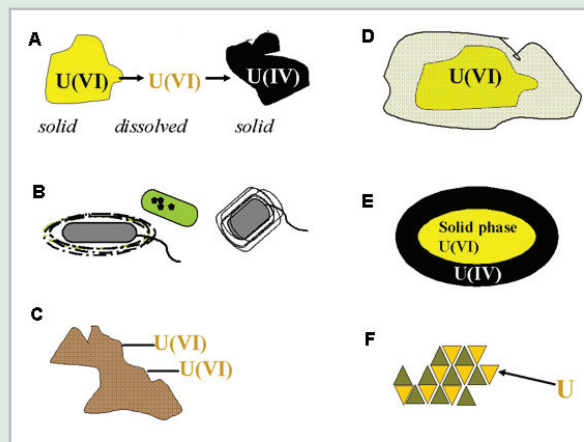


Figure 1. Mechanisms by which U mobility can be retarded in the surface and subsurface geologic environment. A) Precipitation of U(VI) and U(IV) phases. B) Microbial uptake (internal or external) of U. C) The sorption of U by organic or inorganic material such as humic acids and Fe oxides (respectively). D) Occlusion of U by clay and metal oxide coatings. E) Under reducing conditions, the formation of surface rinds of U(IV) on U(VI) minerals can also limit U mobility because U(IV) solids are less soluble. F) Co-precipitation of U with amorphous and crystalline host minerals may limit U mobility (adapted from Duff, Coughlin and Hunter, Uranium Co-precipitation with Fe Oxide Minerals. *Geochim. Cosmochim. Acta*, 66, 3533-3547 (2002).)

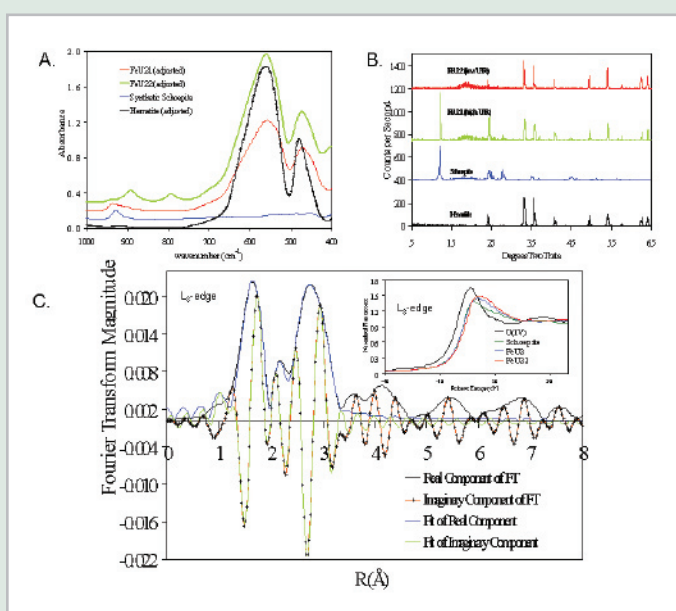


Figure 2. (A) Uranium XAFS spectra (L_3 edge) Fourier transform and fit data for the U-Fe oxide co-precipitate sample, FeU22. Inset: The U XANES spectra (L_3 edge) for U(IV)O₂, the U(VI) mineral meta-schoepite, the FeU2 and FeU22 U-Fe oxide co-precipitate samples. The XANES spectra for uranyl nitrate contained post-edge multiple scattering resonance (MSR) features typically observed for uranyl-containing solids (data not shown). (B) FTIR spectra for hematite, the synthetic U-Fe oxide co-precipitates (FeU21 and FeU22) and the synthetic mineral meta-schoepite. Three of the spectra for the samples are adjusted linearly so that their absorbance peaks are proportional to that of meta-schoepite and (C) Powder X-ray diffraction spectra for hematite, the synthetic U-Fe oxide co-precipitates and the synthetic (adapted from Duff, Coughlin and Hunter, 2002).